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A REFERENCE ELECTRODE FOR USE IN DIMETHYL SULFOXIDE THALLIUM AMALGAM -  
THALLOUS CHLORIDE

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William H. Smyrl and Charles W. Tobias

February 1966

A REFERENCE ELECTRODE FOR USE IN DIMETHYL SULFOXIDE:  
THALLIUM AMALGAM - THALLOUS CHLORIDE

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The measurement of thermodynamic properties of electrolytes and the study of electrode processes in dimethyl sulfoxide (DMSO) requires a suitable reference electrode of the second kind. Solubility studies<sup>1,2,3,4</sup> have shown the chlorides, bromides, iodides, nitrates, and perchlorates to be the most soluble salts in DMSO. Sulfates, fluorides, and carbonates were found to be generally insoluble. For practical reasons the choice of a halide couple would be most advantageous since it affords the establishment of concentration cells without transference.

The silver-silver chloride electrode was explored for use in DMSO by Kolthoff and Reddy<sup>5</sup>, who found that silver chloride is quite soluble in excess chlorides. In this laboratory silver iodide and silver bromide were found to dissolve in excess iodide and bromide, respectively, thereby eliminating the silver-silver halide electrodes from consideration as reference electrodes.

The other obvious choices, the analogues of the calomel electrode, were shown to be unsuitable because mercurous chloride, bromide, and iodide each disproportionate in DMSO. After the salts have been in contact with the solvent for a short time, small droplets of mercury appear in the bottom of the vessel. Analysis of the solution has not been made to confirm the presence of the  $\text{Hg}^{+2}$  ion. However, since  $\text{HgCl}_2$ ,  $\text{HgBr}_2$ , and  $\text{HgI}_2$  are highly soluble in DMSO, these products of disproportionation would promise to be quite stable in solution.

Among the metals which form amalgams and are stable with respect to the solvent, thallium appeared promising. Hills<sup>6</sup> discussed the use of the thallium amalgam-thallos chloride reference electrode in liquid ammonia. Since the thermodynamic properties of thallium amalgams are well known<sup>7</sup>, this electrode couple looked promising for our purposes. Solubility studies were initiated and thallos iodide and chloride were found to be sparingly soluble in dimethyl sulfoxide. Excess iodide precipitates thallos iodide from solution. From visual observations, excess chloride does not precipitate  $TlCl$ , nor does any solid  $TlCl$  dissolve. Further, experiments have shown the solubility product of  $TlCl$  in DMSO to be of the order of  $10^{-6}$ .

On the basis of this information exploratory measurements were initiated with a thallium amalgam-thallos chloride reference electrode. Manipulations were carried out in a dry box. The liquid amalgam<sup>a)</sup>, containing approximately  $10^{-2}$  mol fraction thallium<sup>b)</sup>, was introduced into each one of three special cups, to which electrical contact was made by platinum wires isolated from contact with the electrolyte solution by glass tubes. A 1-2 mm layer of thallos chloride<sup>c)</sup> was sprinkled on the amalgam surfaces, the three electrodes were placed into the cell, and the electrolyte was introduced. In the tightly sealed cell an argon atmosphere of 1 atm pressure was maintained throughout the measurements over the solution. The cell was thermostated at  $25 \pm 0.01^\circ C$ .

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a) Mercury: Baker's Analyzed 4-9's purity.

b) Thallium metal: Cominco 6-9's purity.

c) Thallos chloride: Electronic Space Products, Inc., analytical grade.

The solvent, purified by distillation, contained less than 50 ppm moisture as determined by Karl Fischer titration. Measurements were made with four different  $10^{-2}$  molar solutions, containing one of  $\text{LiCl}^{\text{a)}}$ ,  $\text{RbCl}^{\text{b)}}$ ,  $\text{MgCl}_2^{\text{c)}}$ ,  $\text{InCl}_3^{\text{d)}}$ .

The difference in potential between the electrodes was measured by a K-3 potentiometer<sup>e)</sup>, using a galvanometer<sup>f)</sup> of  $4.5 \times 10^{-10}$  A/mm sensitivity to determine balance. The difference in potential between any two of the three electrodes was always found to be less than 0.03 mV, and less than 0.01 mV in the case of solutions containing  $\text{LiCl}$ . Equilibrium was established rapidly and maintained for at least one week, after which a particular test run was discontinued.

Following Ives and Janz<sup>9</sup> the equilibrium was offset by the application of 0-10 mV potential between electrode pairs, also with reversed polarity. The current passed in either direction ranged up to  $2 \times 10^{-7}$  amperes. This was repeated for all combinations of the three electrodes. The current was always found proportional to the applied potential and on no occasion was there a hysteresis effect observed. The current was applied by a constant current power supply<sup>g)</sup>, and was measured by a Sargent Recorder<sup>h)</sup>. The voltage was measured by an electrometer<sup>i)</sup>.

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- a) Baker & Adamson, Reagent Grade, dehydrated by treatment with thionyl chloride.<sup>8</sup>
  - b)  $\text{RbCl}$ : City Chemical Corp., Purified Anhydrous Grade.
  - c)  $\text{MgCl}_2$ : K & K Laboratories, 99.9% purity.
  - d)  $\text{InCl}_3$ : The Indium Corp. of America, 99.99% purity.
  - e) Leeds & Northrup, Model no. 7553.
  - f) Leeds & Northrup, Model no. 2430-D.
  - g) Electronic Measurements Model C 612.
  - h) Sargent Recorder Model M R.
  - i) Keithley Electrometer Model 610R.

On the basis of these findings, the thallium amalgam-thallic chloride electrode appears suitable for thermodynamic measurements in DMSO solutions, and may be recommended for a practical reference electrode. Care must be taken to protect the amalgam from oxidation, and workers should be aware of the toxicity of thallium and its compounds.

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